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Simulation of aerosols and gas-phase species over Europe with the POLYPHEMUS system: Part I—Model-to-data comparison for 2001

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Abstract

This paper aims at presenting a validation of multi-pollutants over Europe with a focus on aerosols. Chemistry-Transport Models are now used for forecast and emission reduction studies not only for gas-phase species but also for aerosols. Comprehensive model-to-data comparisons are therefore required. We present in this paper a preliminary validation study of the POLYPHEMUS system applied over Europe for 2001. The aerosol model is the SIze REsolved Aerosol Model (SIREAM). It is a sectional model that describes the temporal evolution of the size/composition distribution of atmospheric particles containing a mix of black carbon, mineral dust, inorganic species, and primary and secondary organics. In addition to a brief model description, we present an overview of the model validation. A comprehensive set of model-to-data statistics is computed with observational data extracted from three European databases (the EMEP, AirBase and BDQA databases). Model performance criteria are verified for ozone and particulate matter (PM) and its inorganic components. Comparisons of correlations and root mean square errors with those generated by other models run over Europe for 2001 indicate a good performance of the POLYPHEMUS system. Modifications of the system configuration and parameterizations may have a significant impact on error statistics, which may question the robustness of such models. Because large differences exist between databases, the robustness of model-to-data error statistics is also investigated.

Keywords: Aerosol; Monitoring network; Chemistry-Transport Model; Model performance criteria

0. Introduction

Aerosol modeling is a field of growing interest for many reasons. Particles, especially fine particles, have been implicated in adverse effects on human health (e.g. Pope et al., 1995; Hoek et al., 2002). Atmospheric particles also affect the manner in which radiation passes through the atmosphere (Haywood and Boucher, 2000) and represent an uncertain component of the atmospheric response to the increasing emissions of greenhouse gases. The first motivation for better understanding the behavior of atmospheric aerosol is then related to air quality, while the second one is related to climate change.

Many regulations for air quality now focus on particulate matter (PM) mass. This is the case with the EPA standards in the United States and also the case in Europe with the Clean Air For Europe

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(CAFE) procedure. Models are powerful tools to assess the effects of proposed emission reductions on particulate concentrations. In order to have confidence in these models, however, it is necessary to validate them with observational data. In the past decade, numerous studies have been performed to assess the capacity of Chemistry-Transport Models to simulate the composition and spatio-temporal distribution of aerosols at regional and urban scales (e.g. Cousin et al., 2005; Hodzic et al., 2006a; Zhang et al., 2006; Vautard et al., 2007). Several models are now available in Europe and have been validated and compared for gaseous species and sometimes aerosols. Among many others, one can cite EMEP (Simpson et al., 2003), LOTOS-EUROS (Schaap et al., 2004a, b), EURAD (Ackermann et al., 1995), DREAM (Brandt, 1998) and CHIMERE (Schmidt et al., 2001). They have been tested against aerosol chemical and optical (e.g. de Meij et al., 2006; Hodzic et al., 2006b) measurements provided by ground networks and satellite data. Several models were evaluated for a full year over Europe. For example, Schaap et al. (2004a, b) simulated the aerosol distribution over Europe for the year 1995, and Bessagnet et al. (2004) for the year 2001, but they did not take into account sea salt and natural dust emissions. van Loon et al. (2004) intercompared seven models over Europe for the years 1999 and 2001 for ozone, NO_x, inorganic aerosols and their precursors. A specific exercise (the EURODELTA program) has also been carried out in order to analyze the responses of different models to emission changes. In this framework, the models are intercompared and compared to ozone measurements for the year 2001 (van Loon et al., 2007).

POLYPHEMUS is a modeling system that has been developed for forecasts and assessment of emission reduction strategies over Europe. Its novelty is that it is not an "all-in-one" model: it has been designed as a modular system able to host different model configurations and is thus well-suited for ensemble modeling (Mallet and Sportisse, 2006a). It is the basis of the future forecast system of the French Institute for Nuclear Safety (Quélo et al., 2007) and has been involved in operational testing for photochemistry forecasts on the French Prév'air platform since July 2006 (www.prevair.org). A key focus of POLYPHEMUS is devoted to the model sensitivity with respect to emissions (Mallet and Sportisse, 2005). Many topics related to uncertainties have already been investigated with POLYPHEMUS (Mallet and Sportisse, 2006b). POLYPHEMUS has already been applied to aerosol modeling, through its Chemistry-Transport Model (POLAIR3D), in the MICS (Model Intercomparison Study, Phase II) Asia exercise (Sartelet et al., 2007). Previous European studies with POLYPHEMUS have focused on gas-phase chemistry over summer, and this paper is the logical extension to a full year validation with aerosol modeling. In the framework of studying uncertainties of gas-phase and aerosol species related to modifications of the system configuration and parameterizations over a full year, the focus of this paper is a preliminary validation with a model-to-data comparison for the year 2001 over Europe. This comparison is done using different databases to quantify the robustness of model-to-data error statistics.

This paper is structured as follows. A brief description of the POLYPHEMUS system and of the aerosol model SIREAM (SIze REsolved Aerosol Model) are given in the first section. The model validation exercise is presented in Section 1. The POLYPHEMUS system is used for simulating aerosol over Europe for the year 2001. Error statistics for model-to-data comparisons are computed on the basis of observational data given by three different databases (EMEP, AirBase and BDQA). The focus is on inorganic species and PM_{10} due both to model uncertainties and the lack of measured data for secondary organic aerosol. The results are discussed in the third section. The paper ends with a conclusion and the presentation of future work. A companion paper (Part II) is devoted to a sensitivity analysis.

1. Model description

1.1. The *POLYPHEMUS* system

POLYPHEMUS and its Chemistry-Transport Model POLAIR3D have already been used for many applications, e.g. sensitivity analysis of ozone with respect to emissions (Mallet and Sportisse, 2005), modeling of mercury and heavy metals at continental scale (Roustan and Bocquet, 2006). The POLYPHEMUS platform is made of four distinct components:

- Physical parameterizations and preprocessing of input fields (meteorological fields, boundary conditions and emissions) are performed within the ATMODATA library.
- Drivers have been defined in order to handle high-level use of the models, which can be viewed

as black boxes, e.g. a driver for Monte Carlo simulations, a driver for ensemble forecast.

- Models (for instance the Chemistry-Transport Model Polair3D) constitute the third level of the system. Short-range models (puff and gaussian models) and another CTM, Castor (based on Chimere, Schmidt et al., 2001) are also available.
- The last level is composed of postprocessing tools, especially the Python module AtmoPy. This library (which does not depend on the previous components) performs model-to-data comparisons.

Polyphemus is developed with a GNU/GPL license and the source code is downloadable from the web site http://www.enpc.fr/cerea/polyphemus.

1.2. Gas-phase chemistry

The chemical mechanism chosen for the simulation is RACM (Stockwell et al., 1997). Photolysis rates are computed off-line, as done in the photolysis rate preprocessor JPROC of CMAQ (Roselle et al., 1999).

1.3. The SIze REsolved Aerosol Model (SIREAM)

Two aerosol models are hosted by Polyphemus: MAM (a Modal Aerosol Model, Sartelet et al., 2005) and SIREAM (a SIze REsolved Aerosol Model, Debry et al., 2007). Both models rely on the same parameterizations hosted by the AtmoData library (Sportisse et al., 2006). SIREAM is used for this study.

1.4. Deposition and wet scavenging

1.4.1. Gases

The dry deposition velocities are preprocessed by using the parameterization of Zhang et al. (2003). As in Simpson et al. (2003), the surface resistance is modeled following Wesely (1989) for sub-zero temperatures, and the surface resistance of HNO_3 is assumed to be zero for positive temperatures. Below-cloud scavenging (washout) is parameterized following Sportisse and Dubois (2002). During below-cloud scavenging, equilibrium concentrations of soluble gaseous species can be significantly affected by the ion dissociation during dissolution in water. To take this ionization process into account, effective Henry coefficients are computed given the raindrop pH for the following species: SO_2, NH_3, HNO_3, HNO_2 and HCl.

1.4.2. Aerosols

Dry deposition is parameterized with a resistance approach, following Zhang et al. (2001). Below-cloud scavenging is parameterized with the washout coefficient $\Lambda(d_p) = \frac{3}{2} E(D_r, d_p) p_0 / D_r$, with p_0 the rain intensity in ISU ($m\,s^{-1}$), d_p the particle diameter, D_r the raindrop diameter and E the collision efficiency. The representative diameter for the rain is given as a function of p_0 following Loosmore and Cederwall (2004). The raindrop velocity is computed as a function of the raindrop diameter following Loosmore and Cederwall (2004).

In-cloud scavenging (rainout) is parameterized following Roselle and Binkowski (1999).

In the case of a fog, diagnosed as a cloud whose first level is at ground, the fog settling velocity is parameterized following Pandis et al. (1990).

2. Model setup and comparison methodology

2.1. Model simulation characteristics

2.1.1. Domain

Simulations are performed over Europe. The coordinates of the southwestern-most point are (10.75°W, 34.75°N) in longitude/latitude. The domain of simulation covers an area of $33.5° \times 23°$ with a step of 0.5° along both longitude and latitude. Five vertical levels are considered from the ground to 3000 m. The heights of the cell interfaces are 0, 50, 600, 1200, 2000 and 3000 m.

2.1.2. Meteorological data

Meteorological data are provided by ECMWF (31 vertical levels with a horizontal resolution of $0.36° \times 0.36°$ every 3 h). Vertical diffusion is computed using the Troen and Mahrt parameterization (Troen and Mahrt, 1986) within the boundary layer, and using the Louis parameterization (Louis, 1979) above it. For land use coverage the USGS (United States Geological Survey) land cover map (24 categories) is used.

2.1.3. Boundary conditions

For boundary conditions, daily means are extracted from outputs of the global Chemistry-Transport Model Mozart 2 run over a typical year for gas, and from outputs of the Goddard Chemistry Aerosol Radiation and Transport (GOCART Chin

et al., 2000) model for the year 2001 for sulfate, dust, black carbon and organic carbon.

Forty percent of organic carbon is assumed to be primary aerosol. The remaining 60% is equally distributed amongst the eight organic species of SIREAM on a molar basis. Boundary conditions for sea salt are also provided by GOCART, but they are not used because local emissions of sea salt are taken into account in the system.

As recommended in Vautard et al. (2005), boundary conditions of dust are drastically lowered (here divided by 4), because high dust events are very sporadic and the use of mean values may lead to overestimation of dust concentrations.

Boundary conditions for ammonium are deduced from the sulfate boundary conditions by assuming electro-neutrality of sulfate and ammonium. GOCART provides only total concentrations of sulfate and carbon. Therefore they need to be redistributed amongst the five sections of the aerosol module. The GOCART concentrations are assumed to follow a trimodal lognormal distribution of parameters ($N_1 = 8128 \times 10^6\,\mathrm{m}^3$, $d_1 = 0.014\,\mu\mathrm{m}$, $\sigma_1 = 1.92$) for the first mod, ($N_2 = 4633 \times 10^6\,\mathrm{m}^3$, $d_2 = 0.045\,\mu\mathrm{m}$, $\sigma_2 = 1.87$) for the second mode and ($N_3 = 1235 \times 10^6\,\mathrm{m}^3$, $d_3 = 0.162\,\mu\mathrm{m}$, $\sigma_3 = 1.71$) for the third mode. N_i is the number of particles in the mode, d_i the geometric mean diameter and σ_i the geometric standard deviation (Putaud et al., 2003). Integrating this lognormal distribution over each section gives the percentage of the mass to be allocated to each section. For dust concentrations, GOCART provides concentrations for five bins ranging between 0.1 and 10 μm. For each GOCART bin, the percentage of the mass to be allocated to each section is computed similarly to sulfate and carbon. The trimodal lognormal distribution is integrated over each section.

2.1.4. Emission

2.1.4.1. Gases. Anthropogenic emissions are generated with the EMEP expert inventory for 2001. A typical time distribution of emissions, given for each month, day and hour (GENEMIS, 1994) is applied to each emission sector or SNAP (Selected Nomenclature for Air Pollution) category. Except for the SNAP 10 (agriculture), monthly emission and hourly emission factors are applied following Schaap (2003, pp. 4–46). The inventory species are disaggregated into real species using speciation coefficients (Passant, 2002). NO_x emissions are split into 90% of NO (in mass), 9.2% of NO_2 and 0.8% of HONO. SO_x emissions are split into 95% of SO_2 and 5% of H_2SO_4 (in molar concentrations) following Simpson et al. (2003). The aggregation into model species (for RACM) is done following Middleton et al. (1990). Because emissions are assumed to be instantaneously mixed throughout the first mixing layer, and because gradients from surfacic NH_3 emission maybe very strong, the deposition of NH_3 close to sources is underestimated. To account for this effect, 25% of NH_3 emissions are deposited locally (Tsyro, 2001; Loubet et al., 2003). Biogenic emissions are computed as in Simpson et al. (1999). Two-third of terpene emissions are allocated to α-pinene and one-third to limonene (Johnson et al., 2006).

2.1.4.2. Aerosols. Primary particle emissions are usually given in total mass. For example, the EMEP European emission inventory provides yearly quantities for $PM_{2.5}$ and PM_{10} (particles with diameters less than 2.5 and 10 μm respectively) or PM coarse (particles with diameters between 2.5 and 10 μm). These brute data have to be temporally, chemically, and granulometrically speciated. We follow the recommendations of Simpson et al. (2003). The PM coarse fraction is attributed to mineral dust. The $PM_{2.5}$ fraction is first chemically speciated into three species (mineral dust, MD, primary organics aerosols, POA, and black carbon, BC) by emission source category or SNAP code. These three species contribute to about 35% for dust, 45% for POA and 20% for BC of the total $PM_{2.5}$ mass. They are then distributed into two modes (the Aitken and the accumulation modes). The redistribution of the quantities in the model bins is based on the assumption that each bin belongs to one mode. The emissions of a mode are then equally partitioned amongst the bins that are included in this mode. Sensitivity tests (not reported here) show that the distribution of emissions does not have a great influence compared to other sources of uncertainties.

Sea-salt emissions are parameterized following Monahan et al. (1986), which models the generation of sea salt by the evaporation of sea spray produced by bursting bubbles during whitecap formations due to surface wind. This parameterization is valid at 80% relative humidity. To generalize it, the formula is expressed in terms of dry radius, which is assumed to be approximatively half the radius at 80% humidity (Gerber, 1985). The emitted mass of sea salt is assumed to be made of 55.025% of chloride, 39.33% of sodium and 7.68% of sulfate (Seinfeld

and Pandis, 1998). Although based on the composition of sea water (Seinfeld and Pandis, 1998), sea salt is made of only 30.61% of sodium, the percentage of sodium is taken as 39.33% here. In the real atmosphere, cations such as magnesium and calcium would also contribute to the composition of sea salt. Because these cations are not taken into account in POLYPHEMUS, the percentage of sodium is artificially increased to keep the emitted sea-salt particles electro-neutral.

2.2. Error statistics

The simulation is run over the year 2001, and the evaluation is made for both gases and aerosols. Hourly and peak statistics are computed for O_3. Hourly statistics are computed for NO_2, while daily statistics are computed for SO_2, NH_3, HNO_3 and PM (PM_{10}, sulfate, nitrate, ammonium, sodium and chloride).

2.2.1. Measured data

The model results are compared to observational data provided by three databases:

- the EMEP database, available on the EMEP Chemical Co-ordinating Centre (EMEP/CCC) web site at http://www.emep.int;
- the AirBase database, available on the European Environment Agency (EEA) web site at http://air-climate.eionet.europa.eu/databases/airbase;
- The BDQA database (“Base de Données Qualité de l’Air”: the French Data Basis for Air Quality that covers France), information is available at http://www.atmonet.org/.

The location of the stations is given in Fig. 1 for each of the three databases.

The measurement sites of the EMEP network are assumed to be representative of the regional background concentrations (Torseth and Hov, 2003). The AirBase database contains observational data from the European Air Quality monitoring network (EuroAirnet). For our comparisons only the stations labeled as “background” representative have been used. However, it should be kept in mind that “background” does not have exactly the same meaning between AirBase and EMEP. In AirBase, although traffic and industrial stations have been excluded, stations labeled as background may be representative of urban or suburban background stations. The same kind of filter has been applied to data from the BDQA, in which “rural” and “suburban” stations have been retained.

Measurement data used in this paper are given on a daily average basis except for ozone, for which hourly averages are available. Since AirBase contains observational data from several European networks, some time series measurements may be provided by both AirBase and BDQA or EMEP databases.

There are many uncertainties in the observational data. First, some sites may be not representative of background values (not far enough from important emissions). Second, some sites may be strongly impacted by local conditions (for instance orography). Third, the observational error may be large due to artifacts in the measurement methods (we refer for instance to Schaap et al., 2004a for a deeper understanding; a key process is evaporation of the samples, for example).

The aerosol water content is not taken into account in the model-to-data comparisons. Moreover, although the aerodynamic diameter is used for PM_{10} and $PM_{2.5}$ in measurements, the Stokes diameter is used in the modeling and for the comparison to measurements. The discrepancy in the results is not significant as compared to other uncertainties.

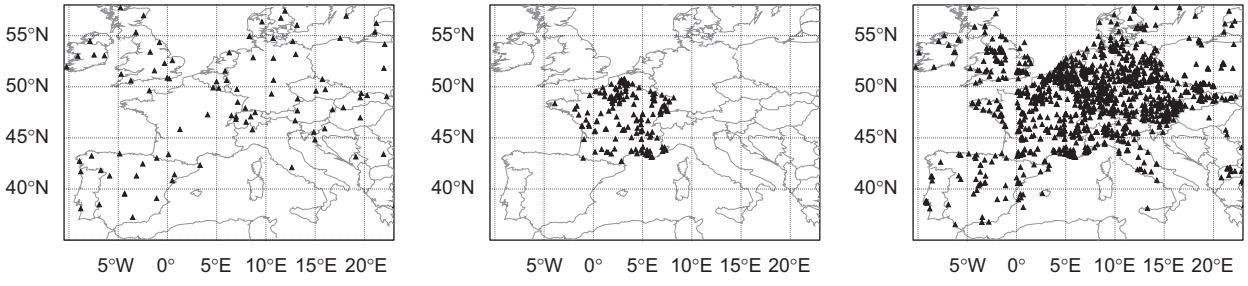

Fig. 1. Locations of the stations for the EMEP (left panel), the BDQA (middle panel) and the AirBase (right panel) databases.

2.2.2. Statistical indicators

The key statistical indicators are the correlation coefficient (%) and the root mean square error (RMSE) ($\mu g\,m^{-3}$) (given in Appendix). The smaller the RMSE and the larger the correlation, the better the model fits the observations. The US EPA (EPA, 1991; Russell and Dennis, 2000) recommends using the mean normalized bias error (MNBE) and the mean normalized gross error (MNGE) with an observation-based minimum threshold of 40–60 ppb (about 80–120 $\mu g\,m^{-3}$) to evaluate hourly ozone. The suggested performance criterion is MNBE $\leqslant \pm 15\%$ and MNGE $\leqslant 30\%$. When computing statistics for ozone in this paper, a threshold of 80 $\mu g\,m^{-3}$ is chosen. Bias indicates whether the model tends to under or overpredict the observations, and error and RMSE indicate how large the deviation is. According to Boylan and Russell (2006), the MNBE and MNGE may not be appropriate to evaluate PM. They suggested using instead the mean fractional bias MFB (%) and the mean fractional error MFE (%). They propose that a model performance goal is met when both the MFE and the MBE are less than or equal to +50% and ±30%, respectively, and a model performance criterion is met when both MFE $\leqslant +75\%$ and MFB $\leqslant \pm 60\%$.

3. Result analysis

3.1. Diurnal cycle of ozone

Fig. 2 shows the yearly mean diurnal cycle of hourly ozone averaged over all BDQA stations and EMEP stations. The model captures very well the diurnal variations of ozone. The peak of ozone in the afternoon is well simulated both in terms of timing and amplitude. At the EMEP stations, the peak is overestimated by 2 $\mu g\,m^{-3}$, while it is underestimated by less than 1 $\mu g\,m^{-3}$ at the BDQA stations. A spread in the amplitude of the ozone peak, as large as 20 $\mu g\,m^{-3}$, is observed by van Loon et al. (2007) which compare seven models for the year 2001. As in van Loon et al. (2007), the spread is larger during night time. At the EMEP stations, the low ozone concentrations are underestimated by 8 $\mu g\,m^{-3}$.

3.2. Spatial distribution

The spatial distribution of pollutants over Europe is shown in Fig. 3 for PM_{10}, $PM_{2.5}$, dust, sea salt, nitrate and ammonium. The spatial distribution of $PM_{2.5}$ shows similar patterns to the distribution computed by Bessagnet et al. (2004) for the year 1999, with high concentrations over northern Italy, the north east of Spain, The Netherlands, Germany and eastern European countries. The spatial distribution of PM_{10} differs from that of Bessagnet et al. (2004), which did not include sea salt and dust. As shown in Fig. 3, the high PM_{10} concentrations observed in the south part of Europe are made mostly of Saharan dust, while the high concentrations in the west part of the domain are mostly due to sea salt.

Fig. 4 shows the simulated gas ratio (GR) (Park et al., 2004)

$$\mathrm{GR} = \frac{[\mathrm{NH}_3^T] - 2[\mathrm{SO}_4^{2-}]}{[\mathrm{HNO}_3^T]}, \tag{1}$$

where concentrations are in molar units, $[\mathrm{NH}_3^T]$ is the sum of ammonium and ammonia, $[\mathrm{HNO}_3^T]$ is the sum of aerosol nitrate and nitric acid and $[\mathrm{SO}_4^{2-}]$ is

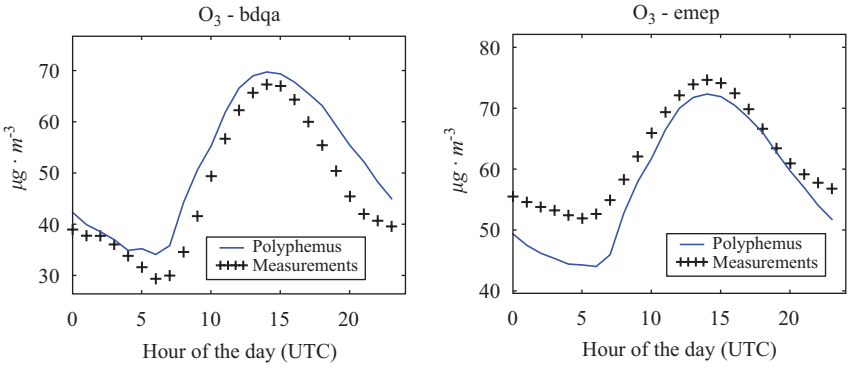

Fig. 2. Yearly mean diurnal cycle of hourly ozone averaged over all BDQA stations (left panel) and EMEP stations (right panel).

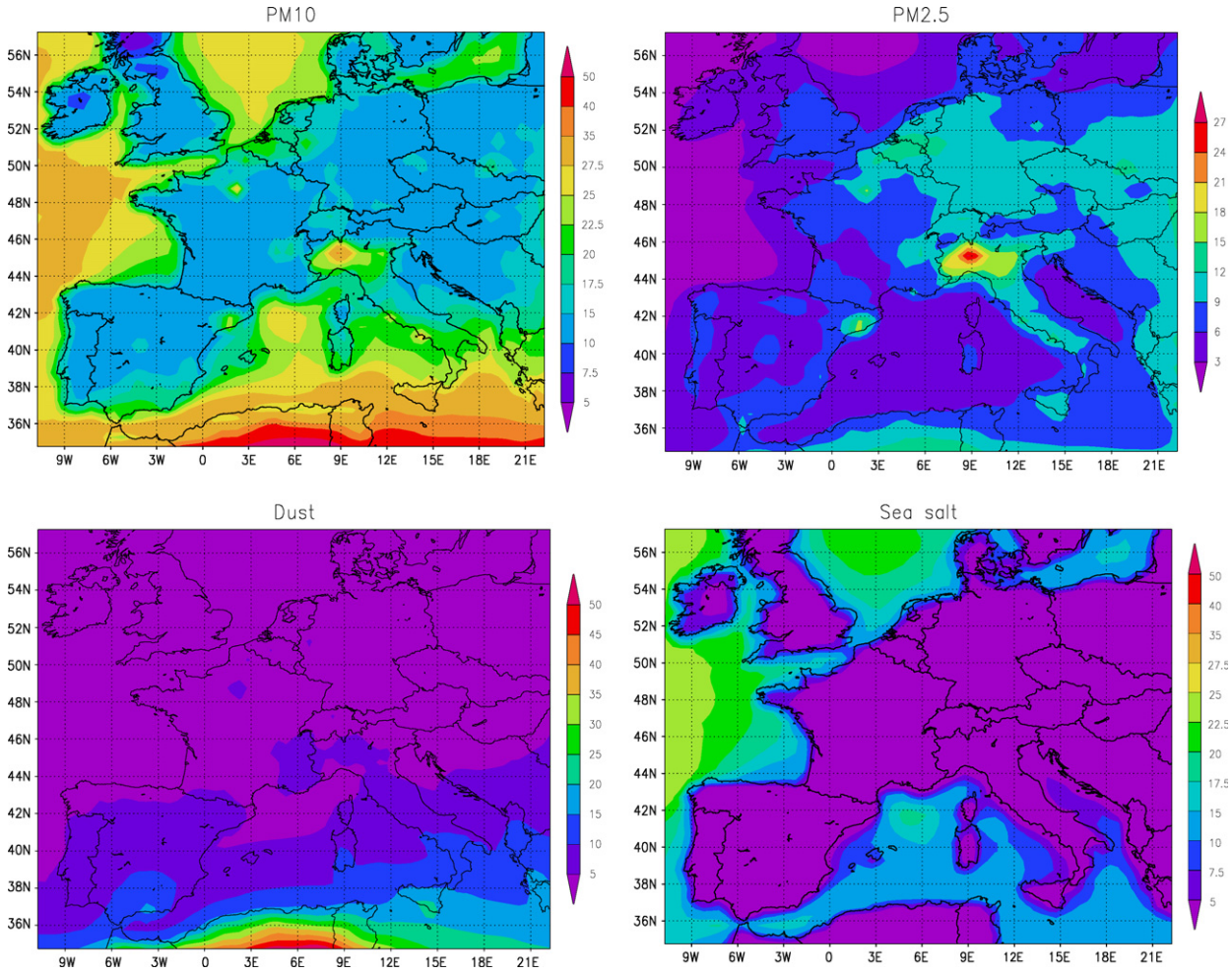

Fig. 3. Yearly mean concentrations (in $\mu g\,m^{-3}$) of PM components in 2001.

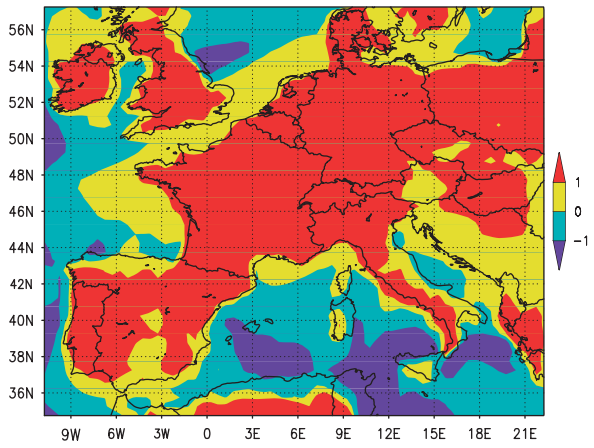

Fig. 4. Mean simulated gas ratio in 2001.

the sulfate concentration. As shown by Park et al. (2004) over the United States, negative GR values, which indicate an acidic sulfate aerosol, are limited to the oceans. Although in Park et al. (2004) over the United States, the supply of ammonia limits the formation of ammonium nitrate ($0<GR<1$), in Europe and especially in western Europe, the ammonium nitrate formation is limited by the formation of nitric acid ($GR>1$).

3.3. Yearly averaged statistics

Statistics obtained with POLYPHEMUS over Europe in 2001 are shown for the three monitoring networks in Tables 1–3.

Statistics strongly vary depending on the observational data network used. For example, NO_2 and SO_2 observed values are, respectively, 2 and 3 times higher with AirBase or BDQA stations than with EMEP stations. These differences stress the importance of the filtering of the stations used for the comparisons. Although urban stations are filtered

out of all databases, stations that are not truly background stations, such as suburban stations, are not filtered out in some databases.

An intercomparison of seven models over Europe for 2001 is presented in van Loon et al. (2004), hereafter referred to as TNO-04. The data used in the report differ from one model to another, e.g. for meteorological data, boundary conditions, emissions, etc. However, it provides a good basis for evaluating the reliability of the results obtained with POLYPHEMUS over Europe for the year 2001. Measurements from both the EMEP and the AirBase databases were used to compute the statistics.

3.3.1. Model performance goal and criterion

The EPA criteria for ozone and ozone peaks are met. Although MNBE goes to values as high as the criterion of ±15%, the MNGE is always largely under the criterion of 30%. For PM_{10}, the model performance criterion is met for the three networks. Furthermore, the results obtained for EMEP and BDQA largely meet the model performance goal, with MFE and MFB well under the thresholds fixed by the goal. Although the criterion was designed for PM_{10} and $PM_{2.5}$, the model performance criterion is met for all aerosol species except chloride. Fig. 5 shows the MFE at each of the EMEP stations for $PM_{2.5}$, sulfate, nitrate and ammonium. For $PM_{2.5}$, the model performance goal is met for only 4 stations out of 17, and the model performance criterion is not met for only 4 stations. Better results are obtained for sulfate and ammonium. For sulfate, 38 stations meet the model performance goal, and only 5 stations out of 57 do not meet the model performance criterion. For ammonium, 7 stations out of 9 meet the model performance goal and only 2 stations out of 9 do not meet the model performance goal and criterion. For nitrate, the results are not as good as for sulfate and ammonium: only 2 stations meet the performance goal, and only 8 stations out of 14 meet the performance criterion. Most of the largest errors correspond to low nitrate concentrations ($\simeq 1\,\mu g\,m^{-3}$).

Table 1
Statistics obtained with POLYPHEMUS over Europe in 2001 for ozone: number of stations used to compute the statistics, observed mean ($\mu g\,m^{-3}$), modeled mean ($\mu g\,m^{-3}$), RMSE ($\mu g\,m^{-3}$), correlation (%), MFB (%), MFE (%), MNBE (%) and MNGE (%)

	O_3 hourly			O_3 peak		
	EMEP	AirBase	BDQA	EMEP	AirBase	BDQA
Stations	96	993	135	96	996	139
Obs. mean	63.2	49.9	53.1	80.2	73.7	77.4
Mod. mean	57.0	53.2	55.5	73.5	72.5	73.7
RMSE	24.3	26.0	25.2	21.4	23.5	23.2
Corr.	63.9	67.5	69.1	72.1	76.5	77.4
MFB	40	12	12	−7	5	1
MFE	−10	55	50	24	31	27
MNBE	−18	−16	−16	−14	−14	−15
MNGE	22	20	20	18	18	18

3.3.2. Comparison to previous intercomparison

For ozone, compared to TNO-04, the observed values reported in Table 1 cover a large range. Values as low as $50\,\mu g\,m^{-3}$ for AirBase and as high as $63\,\mu g\,m^{-3}$ for EMEP are reported. However, the RMSE obtained with POLYPHEMUS are within the low range of those of TNO-04 (24.3–26.0 against 23.1–28.1), and the correlations are slightly higher

Table 2
Statistics obtained with POLYPHEMUS over Europe in 2001 for gaseous species: number of stations used to compute the statistics, observed mean ($\mu g\,m^{-3}$), modeled mean ($\mu g\,m^{-3}$), RMSE ($\mu g\,m^{-3}$), correlation (%), MFB (%), MFE (%)

	Database	Stations	Obs. mean	Mod. mean	RMSE	Corr.	MFB	MFE
NO_2	EMEP	20	10.0	12.3	10.1	33.6	14	70
	AirBase	990	23.9	15.3	18.3	39.5	−38	74
	BDQA	84	21.9	13.8	18.2	38.2	−47	70
NH_3	EMEP	3	7.4	6.3	5.4	29.5	11	52
	AirBase	9	12.9	7.4	12.9	28.4	−21	92
HNO_3	EMEP	7	0.7	1.3	1.4	26.5	36	89
SO_2	EMEP	43	2.0	5.2	4.8	47.5	96	105
	AirBase	956	6.4	6.9	6.5	44.5	22	70
	BDQA	10	7.8	6.6	6.4	36.4	−16	60

Table 3
Statistics obtained with POLYPHEMUS over Europe in 2001 for aerosols: number of stations used to compute the statistics, observed mean ($\mu g\,m^{-3}$), modeled mean ($\mu g\,m^{-3}$), RMSE ($\mu g\,m^{-3}$), correlation (%), MFB (%), MFE (%)

	Database	Stations	Obs. mean	Mod. mean	RMSE	Corr.	MFB	MFE
PM_{10}	EMEP	26	16.9	15.6	12.6	54.5	−7	50
	AirBase	529	24.9	15.4	16.6	44.0	−42	58
	BDQA	23	19.8	15.8	9.6	57.0	−25	40
$PM_{2.5}$	EMEP	17	12.6	8.4	8.6	54.1	−39	61
Sulfate	EMEP	57	2.5	2.1	1.7	55.8	−4	50
	AirBase	11	1.9	2.4	1.6	51.3	41	65
Nitrate	EMEP	14	2.6	4.1	3.1	41.4	32	75
	AirBase	8	3.5	4.4	2.7	71.7	8	54
Amm.	EMEP	9	1.8	2.0	1.3	51.9	20	50
	AirBase	8	1.8	2.0	0.9	74.7	15	36
Sodium	EMEP	3	1.3	3.1	3.0	62.8	67	79
Chloride	AirBase	7	0.9	3.1	3.5	69.8	83	102

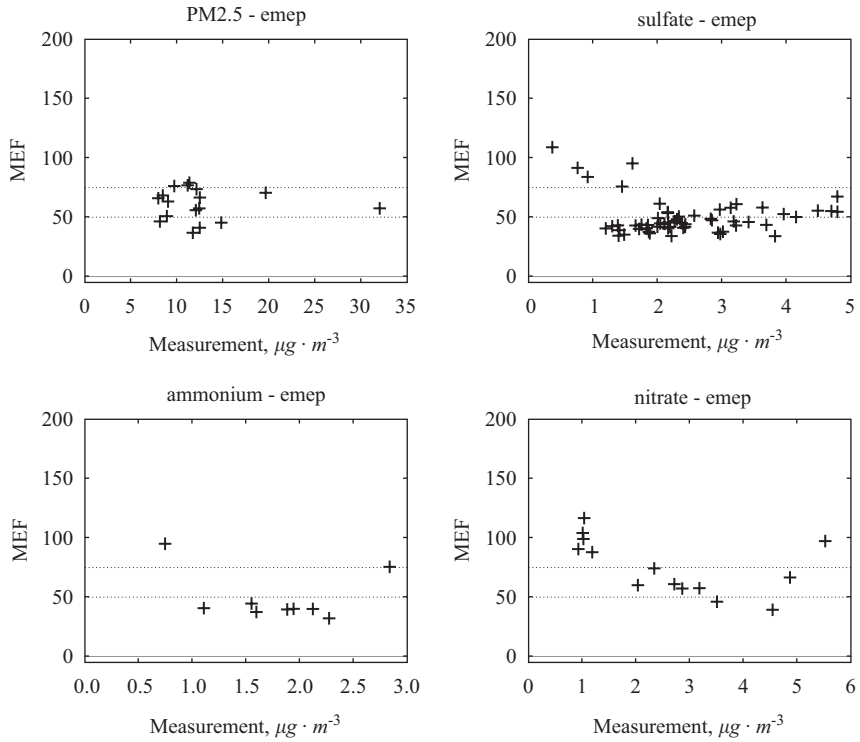

Fig. 5. MFE at each of the EMEP stations for $PM_{2.5}$, sulfate, nitrate and ammonium. The dashed lines represent the model performance goal of 50% and the model performance criterion of 75%.

(63.9–69.1% against 54–59%). This suggests that the results obtained with POLYPHEMUS are comparatively good for hourly ozone. However, for ozone peaks, although the results are good, RMSE obtained with POLYPHEMUS are in the high range (21.4–23.5 against 18.1–22.1) and correlation in the low range (72.1–77.4% against 73–83%).

For NO_2, observed values differ by a factor 2 depending on the network. Good results are observed for the EMEP database with RMSE as

low as 10. However, POLYPHEMUS has difficulties representing the high concentrations observed with AirBase or BDQA. These high concentrations may be explained by suburban stations that have not been filtered out. Note that these high concentrations are much higher than the observed mean of TNO-04 (18 against 15 $\mu g\,m^{-3}$). Accordingly, the RMSE associated with these observations are high. However, correlations are in the same range as those of TNO-04 (33.6–39.5% against 30–46%).

For SO_2, observed values differ by a factor 3 depending on the network. The low SO_2 concentrations observed with the EMEP network are largely overestimated by POLYPHEMUS (2.0 against 5.3). However, the higher concentrations observed with AirBase and BDQA are well represented. If the high concentrations in AirBase and BDQA are explained by suburban stations that are not filtered out, POLYPHEMUS has a tendency to overestimate SO_2 concentrations. The RMSE (4.8–6.5 $\mu g\,m^{-3}$) are in the range of those of TNO-04, which spans from 3.2 to values as high as 10.1 $\mu g\,m^{-3}$, but correlations lie in the low range (36.4–47.5% against 39–49%).

For PM_{10}, the concentrations observed at EMEP stations are lower than those observed at AirBase and BDQA stations (16.9 against 24.9 and 19.8 $\mu g\,m^{-3}$). POLYPHEMUS does not reproduce these high concentrations. In TNO-04, all models tend to underestimate the PM_{10} concentrations. As the range of observed values is large and the observed values of TNO-04 are in the middle of this range, the range of RMSE predicted by POLYPHEMUS is also large (9.6–16.6 against 12.4–15.2 $\mu g\,m^{-3}$). However, the correlations obtained with POLYPHEMUS are in the high range of those of TNO-04 (44–57% against 38–55%).

For sulfate, the concentrations observed with AirBase are slightly lower than the lower observed concentrations of TNO-04 (1.9 against 2.3 $\mu g\,m^{-3}$). The RMSE obtained with POLYPHEMUS are slightly lower (1.6–1.7 $\mu g\,m^{-3}$ against 1.8–2.9 $\mu g\,m^{-3}$), while correlations are in the range of TNO-04 (50–65% against 50–62%).

For ammonium, the observed values as well as the modeled mean and the RMSE are in the range of TNO-04. The correlations obtained with POLYPHEMUS with AirBase are higher (51.9–74% against 44–56%).

For nitrate, the modeled concentrations (4.1–4.4 $\mu g\,m^{-3}$) are higher than those of TNO-04 (1.5–2.9 $\mu g\,m^{-3}$). The RMSE tends to be slightly higher with POLYPHEMUS (2.7–3.1 $\mu g\,m^{-3}$ against a maximum of 2.7 in TNO-04). Correlations are, however, much better with POLYPHEMUS (54–75% against a maximum of 46 in TNO-04).

Although good comparisons of NH_3 concentrations are obtained with the EMEP network, the high NH_3 concentrations (12.9 $\mu g\,m^{-3}$) observed with AirBase are not reproduced by POLYPHEMUS (7.4 $\mu g\,m^{-3}$). HNO_3 concentrations are largely overestimated compared to the EMEP network (0.7 against 1.3 $\mu g\,m^{-3}$).

POLYPHEMUS overpredicts sodium and chloride, especially chloride, even though good correlations with measurements are obtained (63% and 70%). This seems to indicate that the intensity of sea-salt emissions is high. However, the results are very localized: the three stations for sodium are in Denmark and the seven stations for chloride in The Netherlands.

3.3.3. Variability

To illustrate the spatial and temporal variability of the pollutant concentrations, model results versus measurements are plotted at the different EMEP stations for hourly concentrations for O_3 and NO_2 (Fig. 6), and for daily concentrations for PM_{10}, sulfate, ammonium and nitrate (Fig. 7). Very good results are obtained for ozone, with as much as 93.3% of model results that fall within a factor 2 of measurements, and 99.6% that fall within a factor 5. For NO_2, only 50.3% of model results fall within a factor 2 of measurements, but 88.3% fall within a factor 5. For PM, 70.6%, 71.6% and 73.3% of model results fall within a factor 2 of measurements for PM_{10}, sulfate and ammonium, respectively, and 97.5%, 96.5% and 94.6% fall within a factor 5. Larger discrepancies are observed for nitrate with 50.8% of model results that fall within a factor 2 of measurements, and 82.1% within a factor 5.

3.4. Monthly variations

The monthly variations of measured and simulated daily concentrations at the EMEP stations are plotted in Figs. 8 and 9. The results strongly vary with the season. In general, results tend to be better in summer than in winter.

For ozone, best results are observed between April and August when the concentrations are the highest.

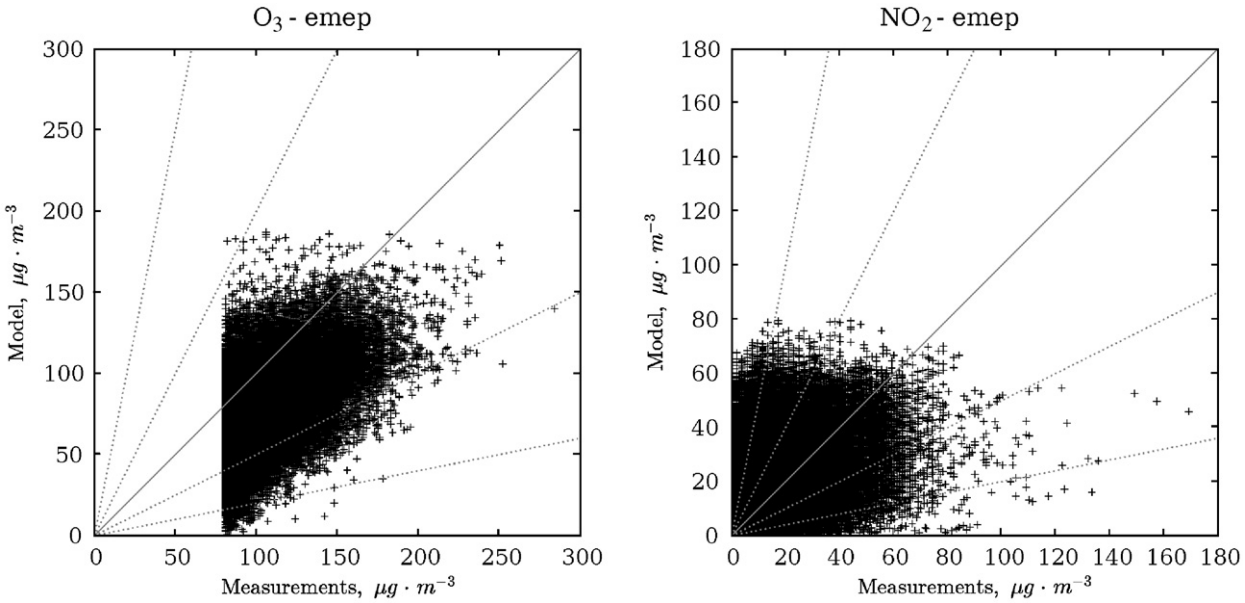

Fig. 6. Model results versus measurements for hourly concentrations at different EMEP stations for O_3 and NO_2. 1:1, 1:2, 2:1, 1:5 and 5:1 reference lines are provided.

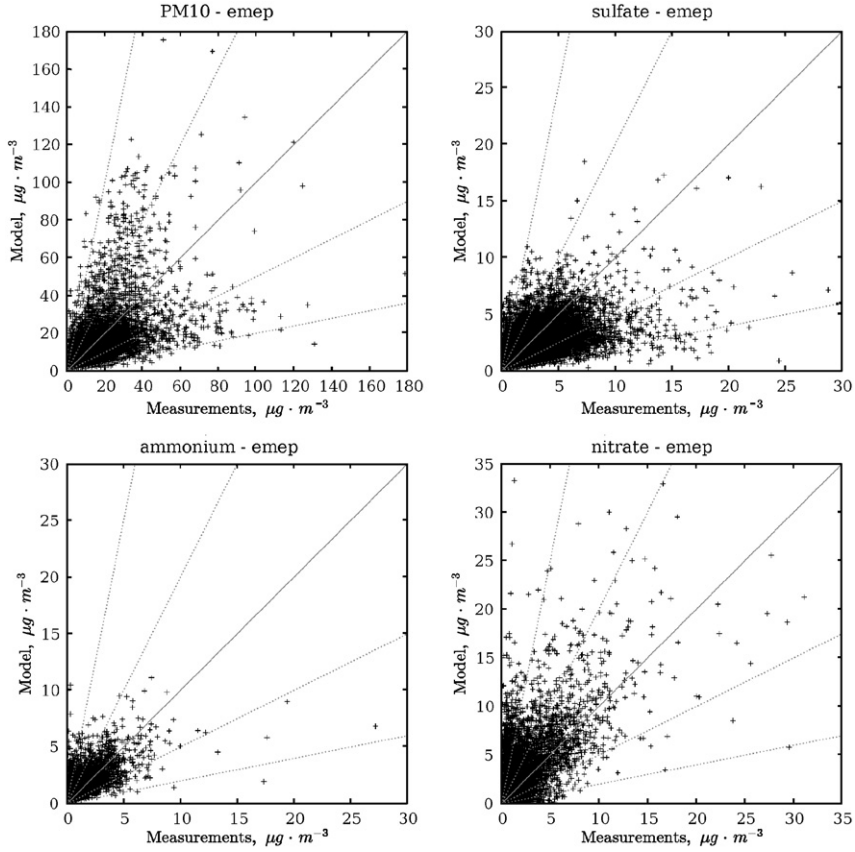

Fig. 7. Model results versus measurements for daily concentrations at different EMEP stations for PM_{10}, sulfate, ammonium and nitrate. 1:1, 1:2, 2:1, 1:5 and 5:1 reference lines are provided.

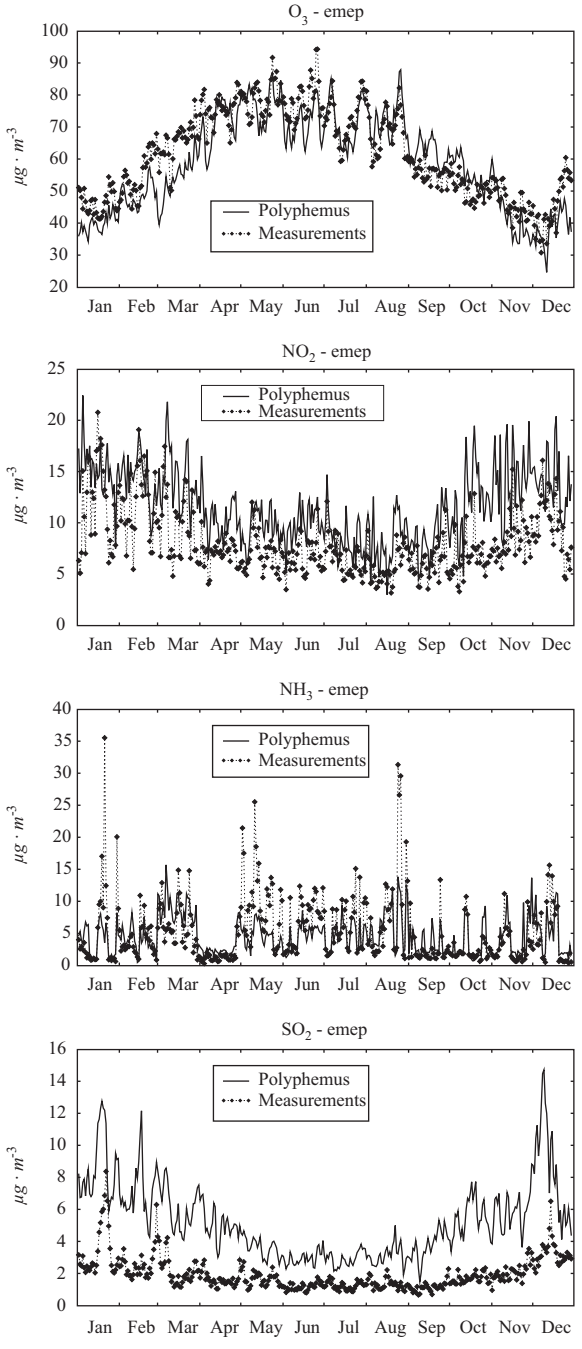

Fig. 8. Time series of daily concentrations of O_3, NO_2, NH_3 and SO_2 at the EMEP stations.

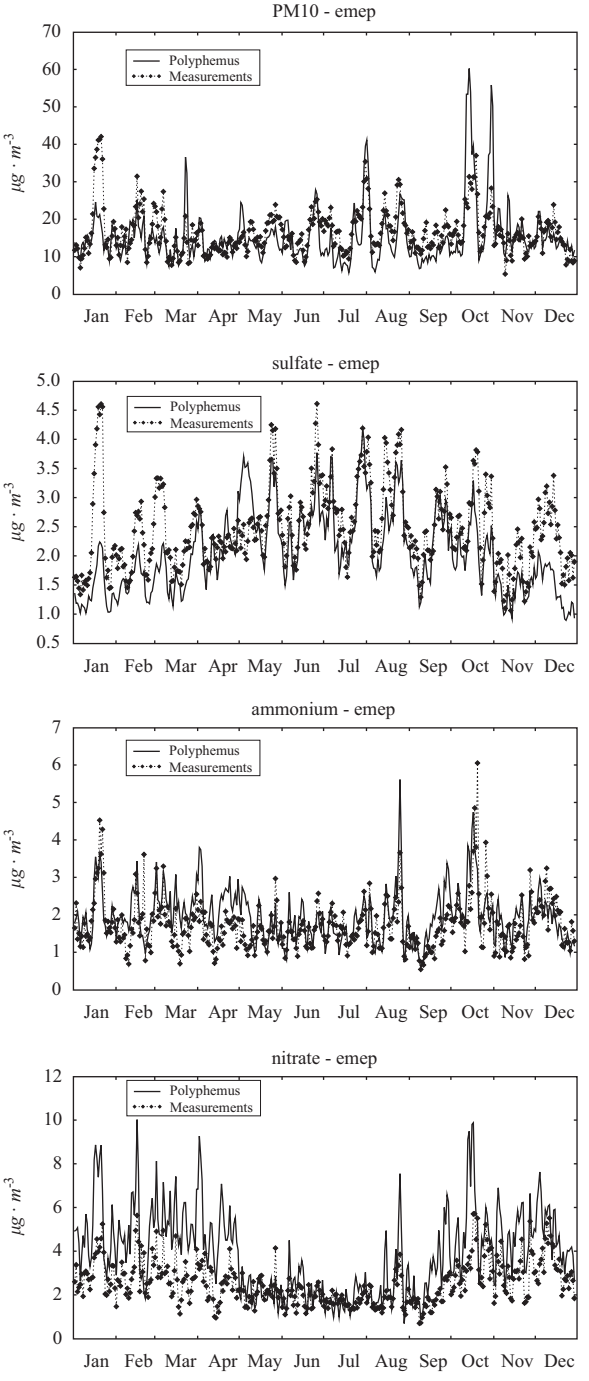

Fig. 9. Time series of daily concentrations of sulfate, ammonium and nitrate at the EMEP stations.

The concentrations of NO_2 tend to be overestimated all through the year, especially during the winter months. Although NO_2 is overestimated at the EMEP stations, it is underestimated at the AirBase and BDQA stations.

NH_3 tends to be underestimated in summer.

For SO_2, best results are obtained between May and August, when SO_2 is not as strongly overestimated as the rest of the year. As for NO_2, the overestimation of SO_2 is not so large at the AirBase

or the BDQA stations compared to the EMEP stations.

PM_{10} tends to be underestimated, except between October and December, where it is slightly overestimated. The underestimation of PM_{10} is larger when looking at the AirBase or the BDQA databases. The underestimation of PM_{10} during the summer months may be explained by the underestimation of secondary organic aerosols. At the EMEP stations, the simulated primary and secondary organic aerosols represent only about 6% of the total aerosol mass, whereas Putaud et al. (2004) estimates the percentage of organics between 16 to 22%. POLYPHEMUS does not take into account all precursors such as isoprene (Henze and Seinfeld, 2006) and sesquiterpenes (Pun et al., 2006a). Some processes such as the oligomerization in the particulate phase, the formation of organics in the aqueous phase (Pun et al., 2006b), the formation of organosulfates (Surratt et al., 2007) and organonitrates are not considered. Another reason of the underestimation of PM_{10} may lie in Saharan dust episodes, which may contribute to daily PM_{10} levels by as much as $20\,\mu g\,m^{-3}$ (Gobbi et al., 2007). Saharan dust episodes are neglected in the simulations and the GOCART boundary conditions for dust are divided by a factor 4. However, at the EMEP stations, the simulated dust represents about 25% of the total aerosol mass, whereas Putaud et al. (2004) estimates the percentage of dust between 9% and 19%. The dust episodes could influence nitrate concentrations. The heterogeneous formation of nitrate on dust particles (e.g. Dentener et al., 1996; Hodzic et al., 2006ba) tends to decrease the HNO_3 concentrations and to increase nitrate concentrations of coarse aerosols in summer.

For sulfate, results tend to be better between June and August. Although SO_2 is strongly overestimated throughout the year in the EMEP database, sulfate is underestimated, especially between October and March. As emphasized by Bessagnet et al. (2004), sulfur aqueous chemistry, which is predominant in winter, is very difficult to simulate, because it is very sensitive to pH. The strong overprediction of nitrate in winter may be explained by the underprediction of sulfate. Because sulfate is underpredicted, more nitrate is required to neutralize ammonium.

For ammonium, the seasonality is not as clear as for other pollutants. It has a slight tendency to be overpredicted in spring. Although NH_3 tends to be underestimated in summer, good results are obtained for ammonium.

3.5. Discussion

The results obtained with POLYPHEMUS for a 1-year simulation over Europe are good. Model performance criteria are met for ozone and particulate species like PM_{10}, sulfate, nitrate, and ammonium. Comparisons of correlations and RMSE with those of other models run over Europe for 2001 point out the strengths and limitations of POLYPHEMUS.

Good results are obtained with POLYPHEMUS for hourly ozone, sulfate and ammonium. Correlations tend to be in the high range for different pollutants such as PM_{10}, sulfate, ammonium, nitrate and even chloride and sodium. However, SO_2 and nitrate concentrations tend to be overestimated.

The robustness of the results obtained with POLYPHEMUS, as an example of CTM, may be questioned. The system is likely sensitive to different parameterizations, inputs, and numerics. Each parameterization or input is likely to influence the pollutants differently in winter and summer. For example, parameterizations related to the aqueous module are more likely to impact aerosol concentrations in winter. On top of differences in ambient conditions, a sensitivity study on modifications of the system configuration and parameterizations may allow us to understand which processes cause pollutants to be overestimated or underestimated, which, as shown above, often depends on the season.

On top of questioning the robustness of the modeling system, one may question the robustness of model-to-data error statistics. Large differences exist between the EMEP and the AirBase measurements, although both databases cover Europe (Fig. 1). For example, the observed mean for O_3 and NO_2 are 63.2 and $10.0\,\mu g\,m^{-3}$, respectively, with EMEP and 49.9 and $23.9\,\mu g\,m^{-3}$, respectively, with AirBase. The observed mean for PM_{10} is $16.9\,\mu g\,m^{-3}$ with EMEP and $24.9\,\mu g\,m^{-3}$ with AirBase. These differences may not only be caused by the observational error due to artifacts in measurement methods but also by the way the stations are filtered in the database. For example, some sites may not be truly representative of background values, and some sites may be strongly impacted by local conditions, such as orography. This difficulty in comparing different database measurements is

reflected in the error statistics, which differ depending on the database used. For PM_{10}, the RMSE is only $12.6\,\mu g\,m^{-3}$ for EMEP, but becomes as high as $16.6\,\mu g\,m^{-3}$ for AirBase.

4. Conclusion and future work

The POLYPHEMUS system has been extended to aerosol modeling by hosting the SIREAM model. The simulation of 2001 over Europe has been studied through an extensive model-to-data comparison for three observational networks (EMEP, AirBase and BDQA). The results, while variable between the chemical species, are good given the results of other such models. The limitations of the model have been pointed out. For example, a more detailed treatment of the formation of secondary organic aerosols is required.

Apart from the conclusions related to the performance of the modeling system, one may question the robustness of such models. A comprehensive sensitivity analysis is required and is the subject of a further paper that investigates the sensitivity of model results with respect to many modeling inputs (physical parameterizations, numerics). Moreover, the error statistics may significantly differ from one network to another, which underlines the difficulty of having fair and robust model-to-data error statistics.

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Appendix A. Statistical indicators

The following indicators are computed by the ATMOPY module in order to evaluate error statistics for model-to-data comparisons. Let $(o_i)_i$ and $(c_i)_i$ be the observed and the modeled concentrations at time and location i, respectively. Let n be the number of data.

We define the following indicators:

- Root mean square error (RMSE):

$$\sqrt{\frac{1}{n}\sum_{i=1}^{n}(c_i-o_i)^2}.$$

- Correlation:

$$\frac{\sum_{i=1}^{n}(c_i-\bar{c})(o_i-\bar{o})}{\sqrt{\sum_{i=1}^{n}(c_i-\bar{c})^2}\sqrt{\sum_{i=1}^{n}(o_i-\bar{o})^2}}$$

with: $\bar{o}=\frac{1}{n}\sum_{i=1}^{n}o_i$ and $\bar{c}=\frac{1}{n}\sum_{i=1}^{n}c_i$.

- Mean normalized bias error (MNBE):

$$\frac{1}{n}\sum_{i=1}^{n}\frac{c_i-o_i}{o_i}.$$

- Mean normalized gross error (MNGE):

$$\frac{1}{n}\sum_{i=1}^{n}\frac{|c_i-o_i|}{o_i}.$$

- Mean fractional bias (MFB):

$$\frac{1}{n}\sum_{i=1}^{n}\frac{c_i-o_i}{(c_i+o_i)/2}.$$

- Mean fractional error (MFE):

$$\frac{1}{n}\sum_{i=1}^{n}\frac{|c_i-o_i|}{(c_i+o_i)/2}.$$

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